



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

THE AGENCY OF MANGANESE IN THE SUPERFICIAL ALTERATION AND SECONDARY ENRICHMENT OF GOLD DEPOSITS¹

WILLIAM H. EMMONS

I. INTRODUCTION AND SUMMARY

Ferric iron, cupric copper, and manganic manganese are present in many mineral waters, and under certain conditions any one of them will liberate chlorine from sodium chloride in acid solutions. Nascent chlorine dissolves gold. Each of these compounds releases chlorine at high temperatures, or in concentrated solutions. In cold, dilute acid chloride solutions, ferric iron will not give nascent chlorine in appreciable quantity in 34 days, and cupric copper is probably even less efficient; but manganic compounds liberate chlorine very readily. In a cold solution containing only 1,418 parts of chlorine per million, considerable gold is dissolved in 14 days when manganese is present. It should be expected, then, that those auriferous deposits, the gangues of which contain manganese, would show the effects of the solution and migration of gold more clearly than non-manganiferous ores.

Gold thus dissolved is quickly precipitated by ferrous sulphate. It is, therefore, natural to suppose that gold in such solutions could not migrate far through rocks containing pyrite, since it would be precipitated by the ferrous sulphate produced through the action of oxidizing waters, or the gold solution itself, upon the pyrite. But the dioxide and higher oxides of manganese react immediately upon ferrous sulphate, converting it to ferric sulphate, which is not a precipitant of gold. Consequently, manganese is not only favorable to the solution of gold in cold, dilute mineral

¹ Published, in a more amplified form, by permission of the Director of the U.S. Geological Survey in *Bull. 46, American Institute of Mining Engineers*, 768-837, October, 1910.

waters, but it also inhibits the precipitating action of ferrous salts, and thus permits the gold to travel farther before final deposition.

These statements apply to the action of surface waters descending through the upper parts of an auriferous ore deposit, since such waters are cold, dilute, acid (i.e., oxidizing) solutions. In deeper zones, where they attack other minerals, they lose acidity, until the manganese compounds, stable under oxidizing conditions, are precipitated together with the gold. Thus, manganite, as well as limonite and kaolin, is frequently found in secondary (i.e., dissolved and reprecipitated) gold ores. Moreover, in the precipitation of secondary copper and silver sulphides, ferrous sulphate is generally formed; and, consequently, the secondary silver or copper sulphides frequently contain gold.

Those deposits in the United States in which a secondary enrichment in gold is believed to have taken place are, almost without exception, manganiferous. Since secondary enrichment is produced by the downward migration, instead of the superficial removal and accumulation, of the gold, it should follow that both gold placers and outcrops rich in gold would be found more extensively in connection with non-manganiferous deposits; and this inference is believed to be confirmed by field-observations.

Among the papers which treat the superficial alteration and secondary enrichment of copper, gold, and silver deposits are those of S. F. Emmons,¹ Weed,² Penrose,³ Winchell,⁴ Van Hise,⁵ Kemp,⁶ and Rickard.⁷ The processes upon which the changes depend are clearly outlined in these, and subsequent work has, in a large measure, confirmed the premises stated. The chemical

¹ "The Secondary Enrichment of Ore-Deposits," *Trans.*, XXX, 177-217 (1900).

² "The Enrichment of Gold and Silver Veins," *Trans.*, XXX, 424-48 (1900).

³ "The Superficial Alteration of Ore-Deposits," *Journal of Geology*, II, No. 3, 288-317 (Apr.-May, 1904).

⁴ *Bulletin of the Geological Society of America*, XIV, 269-76 (1902).

⁵ "Some Principles Controlling the Deposition of Ores," *Trans.*, XXX, 27-177 (1900).

⁶ "Secondary Enrichment in Ore-Deposits of Copper," *Economic Geology*, I, No. 1, 11-25 (Oct.-Nov., 1905).

⁷ "The Formation of Bonanzas in the Upper Portions of Gold-Veins," *Trans.*, XXXI, 198-220 (1901).

laws and physical conditions controlling secondary enrichment have been reviewed in several reports more recently published. The papers of Lindgren, Ransome, Spencer, Boutwell, Irving, Graton, McCaskey, Spurr, and Garrey and Ball are particularly valuable. Such work has shown that the secondary enrichment of pyritic copper deposits is a very important process; that many silver deposits are enriched by superficial agencies; but that many gold deposits do not show deep-seated secondary enrichment.

T. A. Rickard¹ has brought out clearly the processes by which gold deposits may be enriched relatively near the surface in the oxidized zone by the removal of valueless minerals which are more readily dissolved than gold. On the problem of deeper-seated precipitation of gold below the zone of oxidation there is less evidence. In some mines, however, the transportation and deep-seated precipitation of gold is clearly shown, as was pointed out long ago by Weed.

While engaged in the investigation of certain auriferous deposits in the Philipsburg quadrangle, Montana, for the U.S. Geological Survey, I was confronted by evidence gained in two important mines, which seemed to be conflicting on this point. In one of them, the Cable mine, there was no evidence that gold had been concentrated by cold solutions below the zone of oxidation, but in the Granite-Bimetallic Lode there was enrichment of both gold and silver below the zone of leached oxides.

Although the ores of the two deposits differ in other respects, the most striking difference is in the manganese content. The use of manganese in the chlorination process to give free chlorine, which dissolves gold, is well known. Le Conte² said as early as 1879 that free chlorine is the most important natural solvent of gold, and Pearce, in 1885, recorded experiments in which gold had been dissolved in hot sulphate solutions with common salt and manganese dioxide.³ Don obtained similar results with more dilute solutions.⁴ It appeared desirable, therefore, to ascertain whether these reactions are carried on in cold dilute solutions

¹ *Op. cit.*

² *Elements of Geology*, p. 285.

³ *Proceedings of the Colorado Scientific Society*, II, 3 (1885-87).

⁴ *Trans.*, XXVII, 654 (1897).

similar to mine waters; and Nicholas Sankowsky and Clarence Russell, in a seminar on the Chemistry of Ore Deposits, which I conducted at the University of Chicago, compiled all available analyses of waters from gold and silver mines in non-calcareous rocks. A. D. Brokaw conducted a series of experiments, using cold dilute solutions of compositions suggested by the analyses. He performed other experiments applicable to the study of the precipitation of gold, showing the action of manganese dioxide on ferrous salts. During the progress of this investigation, W. J. McCaughey published his valuable paper on the solvent effect of ferric and cupric salt solutions upon gold,¹ and this in a large measure supplemented the work carried on in the seminars at the University of Chicago.

The experiments conducted by Brokaw showed that manganese in the presence of chlorides and sulphates is very much more efficient in the reactions dissolving gold than are the other salts common in mine waters. To verify these results by field-evidence, the review of the literature was taken up in greater detail, and there also the results indicate a marked difference in the behavior of the cold dilute mineral waters in the presence and in the absence of manganese.

Lindgren's classification of the gold deposits of North America has been of great value in reviewing these deposits; since in the United States manganese is rarely a gangue mineral in the primary gold deposits as old as the early Cretaceous California gold veins, whereas it is frequently present in appreciable quantities in those deposits which were formed nearer the surface and which are related to intrusives of Tertiary age.² I have not attempted to review exhaustively the evidence afforded by deposits outside of the United States with respect to the hypothesis suggested, but some of these deposits appear to supply accurate confirmatory data.

In a statistical study of outcrops, to ascertain whether gold is more extensively leached in manganiferous lodes than in the

¹ *Journal of the American Chemical Society*, XXXI, No. 12, 1261-70.

² W. Lindgren, "The Relation of Ore-Deposition to Physical Conditions," *Economic Geology*, II, No. 2, 105-27 (Mar.-Apr., 1907).

outcrops of those which do not carry manganese, and whether placers are more frequently developed in connection with non-manganiferous lodes, the reports of Dr. R. W. Raymond¹ have been of great value.

I wish to acknowledge my indebtedness to my colleagues of the U.S. Geological Survey, and to many other geologists whose accurate observations I have drawn upon to test the hypothesis. Their conclusions respecting the secondary enrichment of gold appear to support the hypothesis, and, differing as they do with respect to the migration of gold in particular deposits, they become reconciled when inspected from this viewpoint, and thus they are themselves supported. Dr. R. C. Wells has read critically certain portions of this paper, where the principles of physical chemistry are involved.

II. SALTS CONTAINED IN THE WATERS OF GOLD AND SILVER MINES IN NON-CALCAREOUS ROCKS

Sankowsky and Russell, utilizing all data available to them, recalculated the analyses to the ionic form of statement, and made the general average given in Table I.

Sulphates.—Primary gold ores generally carry pyrite, which, oxidizing at or near the surface, yields ferrous sulphate, ferric sulphate, and sulphuric acid. The acid is not formed directly from galena, PbS, or from zinc-blende, ZnS; but pyrite, FeS₂, carries more sulphur than is required to supply SO₄ to satisfy the iron, even if ferric sulphate, Fe₂(SO₄)₃, is formed instead of FeSO₄. As shown by Buehler and Gottschalk, galena and zinc-blende dissolve much more slowly in the absence of FeS₂. The reaction probably requires free acid, which the iron sulphide, owing to its excess of sulphur, supplies. The sulphuric acid from pyrite is increased also by the hydrolyzation of ferric sulphate, and the deposition of limonite.

In Table I the sulphate radical is nearly ten times as great as all other negative ions and is also in excess of bases, so that on any basis of adjustment to form salts much H₂SO₄ remains. The table shows also an average of 97.26 parts per million of hydrogen, indicating the strongly acid character of the solutions.

¹ *Mines and Mining West of the Rocky Mountains* (1868-75).

Chlorides.—Chlorine is present in most mine waters. In 22 out of the 29 analyses it is reported as traces or as determined quantities. The average of 29 analyses shows 873 parts per million, but if the one abnormally rich sodium-chloride water of Silver Islet, Lake Superior, is excluded, the remaining 28 analyses show but 111 parts per million. This figure is probably a better average. There are several sources of the chlorine in mine waters.

TABLE I

AVERAGE OF 29 ANALYSES OF WATERS TAKEN FROM GOLD, SILVER, AND GOLD-SILVER MINES IN NON-CALCAREOUS ROCKS
(Compiled by N. Sankowsky and C. Russell)

	Parts per Million	Number of Determinations
Cl ^a	873.10	22
SO ₄	7,292.29	13
CO ₃	77.59	7
NO ₃ ^a	0.06	1
PO ₄	0.00	traces in 2
SiO ₂	34.94	
K.....	17.25	7
Na ^a	261.20	9
Li.....	0.10	1
Ca.....	295.00	11
Sr.....	0.06	1
Mg.....	242.44	9
Al.....	333.65	6
Mn.....	30.91	6
Ni.....	trace	traces in 3
Co.....	trace	
Cu.....	5.09	
Zn.....	2.70	5
Fe ⁱⁱ	277.66	22
Fe ⁱⁱⁱ	603.07	25
H (in acids).....	97.26	10

The salt in sedimentary rocks may be dissolved by ground-water. From the available analyses it appears that this source is of less importance than would be supposed. The chlorine content of composite samples of 78 shales and of 253 sandstones was only a trace, while an analysis of a composite of 345 limestones showed only 0.02 per cent.¹ In some rocks chlorine is present probably as NaCl in the solid particles contained in fluid inclusions. The work of R. T. Chamberlin, A. Gautier, and others has shown that many granular igneous rocks, when heated to high temperatures,

¹ F. W. Clarke, *Bulletin No. 330, U.S. Geological Survey*, 27 (1908).

give off gases equal to several times their own volume. While further inquiry of this character is desirable, it is probably true that in general but little chlorine is present in such gases. But gases from certain volcanic rocks, such as obsidian, often contain a high proportion of chlorine and chlorides. Albert Brun¹ has shown that some of the Krakatoa lavas yield gases which equal about one-half the volume of the rock, and that more than half of such gases consist of chlorine, hydrochloric acid, and sulphur monochloride. The average chlorine content of igneous rocks is, according to F. W. Clarke, 0.07 per cent.

Chlorine is present in nearly all natural waters. Its chief source is from finely divided salt or salt water from the sea and from other bodies of salt water. The salt is carried by the wind and precipitated with rain.² The amount of chlorine in natural ponded waters varies with remarkable constancy with the distance from the shore. The isochlores parallel the shore line with great regularity, as shown by the map in Jackson's report. The chlorine contributed from this source even near the seashore appears small; but it may be further concentrated in the solutions by evaporation or by reactions with silver, lead, etc., forming chlorides, which in the superficial zone may subsequently be changed to other compounds. Penrose,³ discussing the distribution of the chloride ores, pointed out long ago that they form most abundantly in undrained areas.

Carbonates and alkaline earths.—The analyses in Table I do not include those from mines in limestones. The carbonate reported gives an average of 77 parts per million. Even in igneous rocks considerable calcium (295 parts per million) and magnesium (242 parts) are carried by the waters. They are derived in part from reactions between the acid sulphates and the silicates of the wall-rock.

¹ "Quelques recherches sur le volcanisme aux volcans de Java. Cinquième partie. Le Krakatau," *Archives des sciences physiques et naturelles*, Genève, XXVIII, No. 7 (juillet, 1909).

² D. D. Jackson, "The Normal Distribution of Chlorine in the Natural Waters of New York and New England," *Water Supply and Irrigation Paper No. 144, U.S. Geological Survey* (1905).

³ *Journal of Geology*, II, No. 3, 314 (April-May, 1894).

Alumina.—In some waters aluminum sulphate is abundant (the average of aluminum, 333 parts per million). It forms where sulphate waters attack kaolin, setting free SiO_2 and taking alumina into solution.

Nitrates.—Nitrates are not abundant in mine waters. In one analysis only¹ is NO_3 reported (1.60 parts per million), and this in a deep-seated water of questionable genesis.

Phosphates.—Traces only of PO_4 are reported from two mine waters; others contained none, if determinations were made.

Silica.—Silica (35 parts per million) appears high for acid waters. The analyses include a manganiferous sulphate water from the Comstock, abnormally high in silica.²

Iron.—Iron is the most abundant metal in the waters of gold mines. Ferric iron (603 parts per million) is, according to these analyses, more than twice as abundant as ferrous iron (277 parts per million). Ferrous iron is much more abundant below than above the water-table.

Manganese.—If manganiferous minerals are present in the primary ore, they oxidize in the upper portion of the deposit to manganese dioxide or other high oxides of manganese; and these, in turn, oxidize ferrous sulphate, in the presence of sulphuric acid, to ferric sulphate.

Copper.—One analysis shows 147 parts of copper per million. Two other analyses show traces. Small amounts must be present in many other waters, since gold ores often carry copper. Possibly, small traces of the heavy metals were not looked for in many of the waters analyzed.

III. CHEMICAL EXPERIMENTS IN THE SOLUTION AND DEPOSITION OF GOLD

The migration of gold in the deposits takes place at low temperatures. At the surface the temperatures range between 0° and 50° C. and pressures do not exceed one atmosphere. With the normal gradient of increase, the temperatures, even several

¹ Geyser Mine, Silver Cliff, Colo. See S. F. Emmons, *Seventeenth Annual Report, U.S. Geological Survey, Part II*, 462 (1895-96).

² *Bulletin of the Department of Geology, University of California*, IV, No. 10, 192 (1904-6).

thousand feet below water level, would not exceed 100° C., and in the main are considerably lower. The general character and, approximately, the concentration of the solutions are known and the conditions are fairly constant. From the mass of chemical data relating to the subject, the following experiments are particularly suggestive in connection with the present problem.

1. Stokes¹ placed gold leaf in a solution containing 25 gm. per liter of ferric sulphate, and, after heating to 200° C., found that not a trace of gold had been deposited in the cold part of the sealed tube in which the experiment was carried on. This experiment does not confirm the statement frequently made that ferric sulphate will dissolve gold.

2. Don² exposed to air, gold and auriferous sulphide ores in solutions containing from 1 to 20 gm. of ferric chloride and ferric sulphate per liter of water; after several months no gold had been dissolved.

3. W. J. McCaughey,³ upon boiling for several hours 50 c.c. of HCl (sp. gr. 1.178) diluted to 125 c.c. with 250 mg. of gold, found there was no loss of gold.

4. In a bent tube Stokes⁴ heated gold leaf for 16 hours at 200° C. in a solution composed of 85 gm. of cupric chloride and 133 c.c. of 20 per cent HCl in a liter of water. The gold leaf was dissolved and redeposited in the upper portion of the tube. He writes the reaction as follows:



5. Stokes⁵ heated gold leaf to 200° C. in a closed tube containing a solution of 25 gm. of ferric sulphate and 0.01 gm. of NaCl. Gold was dissolved in 40 hours.

6. Stokes⁶ found that at 200° C. gold leaf was dissolved in a mixture of 2 parts of 20 per cent solution of ferric chloride and 1 part of 20 per cent solution of HCl.

¹ *Economic Geology*, I, No. 7, 650 (July-Aug., 1906).

² *Trans.*, XXVII, 598 (1897).

³ *Journal of the American Chemical Society*, XXXI, No. 12, 1263 (Dec., 1909).

⁴ *Op. cit.*, I, 649.

⁵ *Economic Geology*, I, No. 7, 650 (July-Aug., 1906).

⁶ *Ibid.*, 650.

7. W. J. McCaughey¹ dissolved gold at from 38° to 43° C., in hydrochloric acid solutions of ferric sulphate. The results are indicated by the curves in Fig. 1. Solution A contained 1 gm. of iron, introduced as ferric sulphate, and 25 c.c. of HCl (sp. gr. 1.178) in a solution diluted to 125 c.c. containing 250 mg. of gold rolled to 0.009 inch. Solution B contained the same amount of iron sulphate and 50 c.c. of HCl. Solution C contained 2 gm. of Fe as ferric sulphate and 25 c.c. of HCl. Solution D had twice

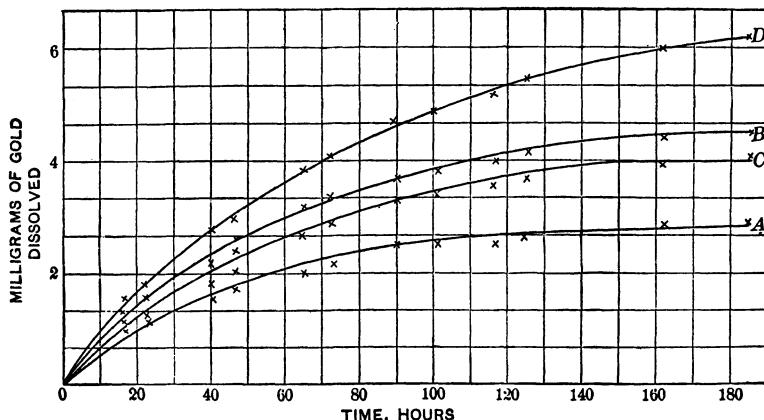


FIG. 1.—Diagram Showing the Rate of Solution of Gold in Concentrated Solutions of Hydrochloric Acid and Ferric Sulphate. (Illustrating Experiment 7, by McCaughey.)

the concentration of A. The diagram shows the amount of gold dissolved after different periods of treatment.

8. McCaughey² found that gold is dissolved at from 38° to 43° C. in a strong solution of cupric chloride and HCl. The amounts dissolved are shown by the curves in Fig. 2. Solution A contained 1 gm. of Cu as cupric chloride and 25 c.c. of HCl (sp. gr. 1.178); solution B, 1 gm. of Cu as CuCl_2 , and 50 c.c. of HCl; solution C, 2 gm. of Cu as CuCl_2 and 25 c.c. of HCl; and solution D, 2 gm. of Cu as CuCl_2 and 50 c.c. of HCl; the final solution being in all cases diluted to the volume of 125 c.c. The

¹ *Journal of the American Chemical Society*, XXXI, No. 12, 1263 (Dec., 1909).

² *Ibid.*, 1264.

diagram shows that *D*, which was twice as concentrated as *A*, dissolved about 12 times as much gold.

9. Richard Pearce¹ placed native gold in a flask containing hydrated manganese dioxide with 40 gm. of salt and 5 or 6 drops of H_2SO_4 . After heating for 12 hours appreciable gold had been dissolved.

10. T. A. Rickard² extracted 99.9 per cent of the gold from manganiferous ore with a solution of ferric sulphate, common salt, and a little H_2SO_4 .

11. Don³ found that 1 part of HCl in 1,250 parts of H_2O , in the presence of MnO_2 , dissolves appreciable gold.

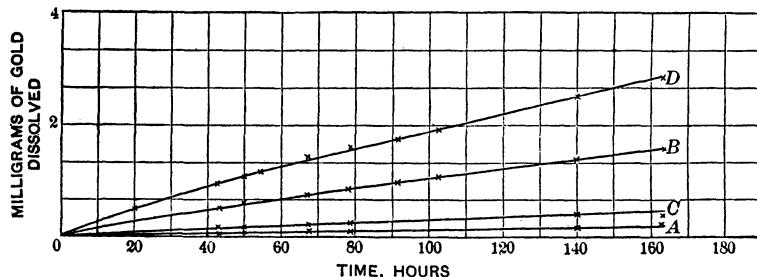


FIG. 2.—Diagram Showing the Solubility of Gold in Concentrated Solutions of Hydrochloric Acid and Cupric Chloride. (Illustrating Experiment 8, by McCaughey.)

A number of experiments on the solubility of gold in cold dilute solutions were made by A. D. Brokaw.⁴ The nature of these experiments is shown by the following statements, in which (*a*) and (*b*) represent duplicate tests:

12. $Fe_2(SO_4)_3 + H_2SO_4 + Au$.
 (a) no weighable loss. (34 days.)
 (b) no weighable loss.

13. $Fe_2(SO_4)_3 + H_2SO_4 + MnO_2 + Au$.
 (a) no weighable loss. (34 days.)
 (b) 0.00017 gm. loss.⁵

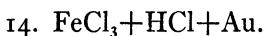
¹ *Trans.*, XXII, 739 (1893).

² *Trans.*, XXVI, 978 (1896).

³ *Trans.*, XXVII, 599 (1897).

⁴ *Journal of Geology*, XVIII, No. 4, 321-26 (May-June, 1910).

⁵ This duplicate was found to contain a trace of Cl, which probably accounts for the loss.



(a) no weighable loss. (34 days.)
 (b) no weighable loss.



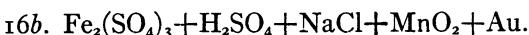
(a) 0.01640 gm. loss. Area of plate, 383 sq. mm. (34 days.)
 (b) 0.01502 gm. loss. Area of plate, 348 sq. mm.

In each experiment the volume of the solution was 50 c.c. The solution was one-tenth normal with respect to ferric salt and to acid. In experiments 13 and 15, 1 gm. of powdered manganese dioxide was also added. The gold, assaying 999 fine, was rolled to a thickness of about 0.002 inch, cut into pieces of about 350 sq. mm. area; and one piece, weighing about 0.15 gm., was used in each duplicate.

To approximate natural waters more closely, a solution was made one-tenth normal as to ferric sulphate and sulphuric acid, and one twenty-fifth normal as to sodium chloride. Then 1 gm. of powdered manganese dioxide was added to 50 c.c. of the solution, and the experiment was repeated. The time was 14 days.



No weighable loss.



Loss of gold, 0.00505 gm.

The loss is comparable to that found in experiment 15, allowing for the shorter time and the greater dilution of the chloride.

To determine whether the free acid or the ferric chloride is the solvent, experiment 17 was made, in which 50 c.c. of one-tenth normal HCl was used with 1 gm. of powdered MnO_2 .



Loss of Au, 0.01369 gm. Time, 14 days.

In experiment 18, sodium hydroxide was added to 50 c.c. of one-tenth normal ferric chloride solution until the precipitate formed barely redissolved on shaking, after which 1 gm. of powdered MnO_2 was added.



Loss of Au, 0.00062 gm. Time, 14 days.

These results show that, in the presence of manganese dioxide, free hydrochloric acid is more efficient than ferric chloride. The same amount of chlorine was present in both solutions.¹

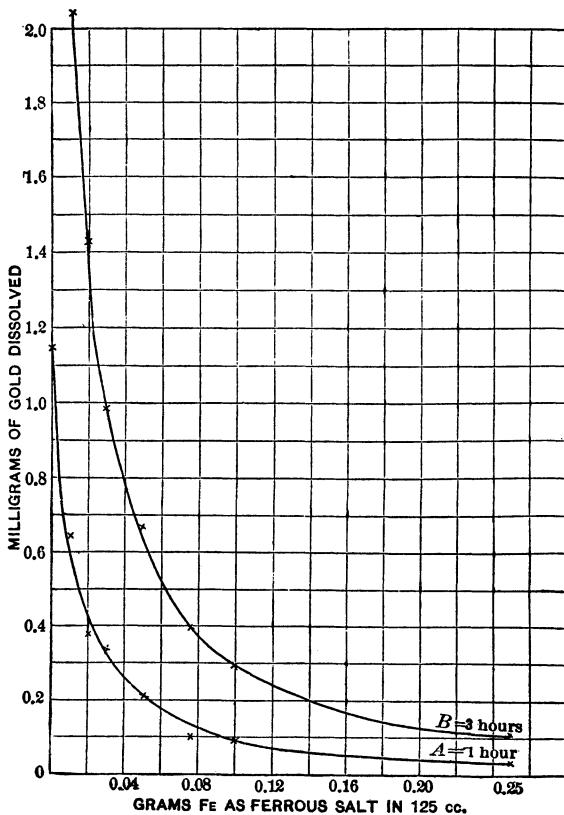


FIG. 3.—Diagram Illustrating the Effect of Ferrous Sulphate in Suppressing the Solubility of Gold in Ferric Sulphate Solutions, where Gold is Dissolved as Chloride. (Illustrating Experiment 19.)

19. McCaughey's experiments show the effect of very small amounts of ferrous sulphate on solutions of gold in ferric sulphate. To a solution, 125 c.c., containing 1 gm. of iron as ferric sulphate and 25 c.c. of HCl, ferrous sulphate was added in quantities containing from 0.01 to 0.25 gm. of ferrous iron. The solutions were immersed in boiling water and subsequently 250 mg. of gold was

¹ Brokaw, *Journal of Geology*, XVIII, No. 4, 322-23 (May-June, 1910).

added. The dissolved gold was determined at the end of 1 hour and 3 hours. At the end of 3 hours the gold dissolved was greater, probably because some ferrous sulphate had changed to ferric sulphate. Even 0.01 gm. of the ferrous iron greatly decreases the solubility of gold in the ferric sulphate and HCl solution, and 0.25 gm. of ferrous sulphate drives nearly all the gold out of solution. These experiments are illustrated by Fig. 3. The lower curve represents conditions at the end of 1 hour, the upper curve at the end of 3 hours, when some of the ferrous salt had oxidized by contact with the air.

20. To determine the rate at which ferrous sulphate, in the presence of sulphuric acid and manganese dioxide, would be oxidized to the ferric salt, Brokaw made the following experiment:

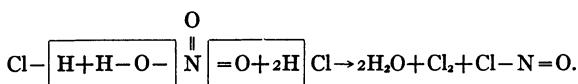
One hundred c.c. of 1.6 normal FeSO_4 was acidified with sulphuric acid and shaken vigorously with 5 gm. of powdered MnO_2 . After 5 minutes the solution was filtered. No ferrous iron was detected by the ferricyanide test, showing that the iron had been completely oxidized to the ferric state.

IV. DISCUSSION OF EXPERIMENTS

Nitrates.—Dilute acid nitrate-chloride waters readily dissolve gold, since they are equivalent to weak aqua regia. The chlorine set free by the reaction oxidizing HCl is more active than a solution of chlorine in water, and converts gold into gold chloride.

In the reaction by which gold is dissolved in chloride solution its solvent power may be ascribed to its “nascent” state. In such reactions the presence of an element with more than one valence is a necessary condition and its valence is reduced as gold passes into solution.

The reaction of $3\text{HCl} + \text{HNO}_3$, giving nascent chlorine, may be written as follows:^x



When nascent chlorine reacts with gold, it forms soluble gold chloride.

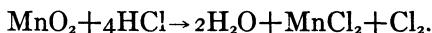
^x Alexander Smith, *General Inorganic Chemistry*, 449 (1907).

In the 29 analyses of mine waters NO_3 is reported from but one. Possibly nitrates are more abundant than is indicated by the analyses; and if so, they must increase the solvent power of chloride solutions; but the data at present available do not indicate that they affect the superficial reactions to any important extent.

Manganese oxides.—That gold is dissolved in moderately dilute solutions containing salt and manganese oxides is shown by experiments 11, 15, and 16. The reaction with manganese used to prepare chlorine commercially is illustrated by the following equation. (The reaction is not so simple as stated. It is discussed later.)



At the beginning of the reaction the manganese has a valence of four; at the end a valence of two. With acid the reaction may be as follows:



Besides the presence of a chloride, some other conditions are essential to the solution of gold. There appear to be two. One is that some other substance must also be present which is capable of being reduced so as to liberate chlorine—as, for example, a ferric salt which may be reduced to the ferrous, a cupric to the cuprous, the higher manganese salts to the lower, etc. The other is the evolution of “nascent” chlorine. This is particularly illustrated by the action of aqua regia or the production of chlorine by hydrochloric acid and pyrolusite. In short, any of a number of methods of producing free chlorine would be effective in the solution of gold. Possibly both of the conditions just mentioned may in the last analysis be identical. The essential point is that the atomic chlorine in a state of molecular exchange or evolution is able to combine with the gold. For present purposes the gold may be considered to dissolve as gold chloride, although chemical investigations favor the theory that a complex ion containing gold is formed. The only consideration which becomes important in its geological aspect is the presence of the compounds which not only

admit of easy changes of valence, but which act upon hydrochloric acid with the production of free chlorine.

In mine waters chlorine is supplied as NaCl.



N/10 N/10 N/25 1 gm. 0.15 gm.

0.00505 gm. loss of gold by solution in 14 days (cold).

Under the same conditions without manganese there was no weighable loss (see experiment 16a).

As used herein the normal solution contains 1 gm.-equivalent of the solute in 1 liter of solution. A solution normal with respect to chlorine contains 1 gm. of chlorine times 35.45, the molecular weight of chlorine, in 1 liter of solution.

In this experiment the concentration of Cl (1,418 parts per million) is not so great as has been observed in a few mine waters, and not more than three times as great as Don determined in waters from a number of Australasian mines.¹

Manganese is abundant in many gold-bearing deposits; is sparingly represented in some; and from a very large number it has not been reported. The chief primary minerals are the carbonates (rhodochrosite and manganeseous calcite), the silicate (rhodonite), amethystine quartz, and the less-abundant sulphide, alabandite. Some rock-making minerals carry small amounts of manganese. It readily forms sulphates, chlorides, etc., and is dissolved by acid mine waters. Manganese changes its valence more readily than other elements common in gold ores.

Lead oxides.—Lead oxide is said to facilitate the solution of gold² when added to solutions of ferric sulphate and sodium chloride. Lead is both bivalent and quadrivalent and forms corresponding oxides and hydroxides. These, however, are generally not abundant in the oxidized zones of lead-bearing ore deposits, because the lead carbonate and the sulphate are relatively insoluble in water and usually are formed instead of the oxides. Lead is reported in but one of the 29 analyses of waters from gold and

¹ *Trans.*, XXVII, 654 (1897).

² Victor Lehner, *Journal of the American Chemical Society*, XXVI, No. 5, 552 (May, 1904).

silver mines, tabulated above. It is believed to be of very subordinate importance in connection with the solution of gold.

The efficiency of ferric iron and cupric copper to supply nascent chlorine, compared with that of manganitic manganese.—Solutions of ferric sulphate with sulphuric acid and salt dissolve gold at high temperatures. Concentrated solutions of ferric sulphate and hydrochloric acid dissolve gold at from 38° to 43° C. In the cold the reaction may go on in concentrated solutions, but in those approximating the concentration of mine waters no weighable loss of gold was obtained. With MnO_2 under the same conditions there was a very appreciable loss in a solution containing only 1.4 gm. of Cl in a liter. It appears, therefore, that the action of ferric iron on gold in cold dilute mine waters with H_2SO_4 and $NaCl$ is probably negligible; for the experiments with ferric iron in such solutions, without manganese, extended over a period of 34 days without weighable loss of gold.

Many auriferous deposits contain copper, but since the reactions which give nascent chlorine are conditioned upon the presence of some element that changes its valence in the reactions, and since the processes underground take place in sulphate solutions, it did not appear necessary, after ferric salt had been shown to be incompetent, to conduct experiments with copper; for, as is well known, cuprous salts have never been detected in acid sulphate mine waters, whereas ferric and ferrous sulphate are very common in such waters. It has been shown¹ however that the efficiency of cupric salt in cold solution compared with that of manganitic salt probably lies somewhere between 0.004 and 0.000001.

Amount of chlorine necessary for the solution of gold with manganese compounds present.—In experiment 15 (a), with MnO_2 , 0.01640 gm. of gold was dissolved in 34 days with solution one-tenth normal with respect to chlorine. A solution with but 40 per cent as much Cl (experiment 16b) dissolved 31 per cent as much gold in 14 days as was dissolved in the more concentrated solution in 34 days. These results show that in 15 (a) conditions are probably approaching equilibrium, and also that the solvent power of chlorine is approximately proportional to the amount present.

¹ *Bull. Amer. Inst. Mining Eng.*, 790 (October, 1910).

That a weighable quantity of gold is dissolved when only a trace of chlorine is present is shown by experiment 13 (6), in which chlorine was introduced without intention.

The precipitation of gold.—In igneous rocks ferrous sulphate is the chief precipitating agent. Ferrous sulphate is formed by the oxidation of pyrite, but in the presence of oxygen and H_2SO_4 , it becomes ferric sulphate, which does not precipitate gold. Below the water-table, where pyrite is more abundant and free oxygen less abundant, ferrous sulphate may persist in the mine waters. Ferrous sulphate is so effective as a precipitant of gold that it is used for that purpose in metallurgical processes. Experiment 19 shows that a minute amount of ferrous sulphate greatly decreases the solubility of gold, although it does not precipitate it completely. With excess of ferrous salt practically all of the gold is precipitated.

Ferrous sulphate is formed in the upper part of a lode above the water-table; but owing to the open condition of that part of the lode, air is freely admitted and ferric sulphate forms, at the expense of ferrous sulphate and sulphuric acid. This reaction takes place almost instantaneously if MnO_2 is present (experiment 20), for ferrous sulphate and manganese dioxide are under these conditions incompatible. *Manganese dioxide then not only releases the solvent for gold, but eliminates the salt which precipitates it.* It is doubtful whether appreciable amounts of gold are ever carried far below the water-table in mines where the waters carry ferrous sulphate, but, in the presence of MnO_2 , ferrous sulphate may be eliminated below the water-table.

When manganese dioxide takes part in the reactions by which, under the conditions named, gold is dissolved, transported, and precipitated, the manganese salt is itself changed. At the surface pyrolusite, MnO_2 , forms, for there the excess of oxygen prevails; and this mineral is commonly found in the gossan of manganiferous lodes. When solutions containing H_2SO_4 and $NaCl$ react on MnO_2 there is a tendency to form $MnSO_4$, and some manganese goes into solution as sulphate, but salts of manganese with higher valence may also form. In this connection Dr. R. C. Wells has offered the following statement:

In an acid solution containing some free chlorine, such as has been assumed to be effective in dissolving gold, there would also be a tendency towards the formation of permanganic acid. On the other hand, the production of the chlorine necessarily results in the reduction of the manganese compound. Now a manganous salt is known to react with permanganate to reproduce MnO_2 and this illustrates the tendency of manganese to pass with ease from one stage of oxidation to another. The precipitation of manganese will occur more and more as the solution loses its acidity. It is well established that manganous salts in an acid environment are very stable; but in neutral or alkaline solutions they oxidize more vigorously, one stage of their oxidation being the manganic salt which hydrolyzes into $Mn_2O_3 \cdot H_2O$ (manganite), with even greater ease than ferric salts into limonite.

In these ways the migration of an acidic solution would result in the transportation of both gold and manganese. But in a region of basic, alkaline, and reducing environment the manganese would be reprecipitated, the free acid neutralized, the chlorine absorbed by the bases and removed, and owing to the accumulation of the ferrous or other reducing salts, the gold would be reprecipitated.

V. THE TRANSFER OF GOLD IN COLD SOLUTIONS

1. *Restatement of the processes as related to secondary enrichment.*

—Every theory of secondary enrichment of the metals consists essentially of three parts: (a) solution, (b) transportation, (c) precipitation.

a) As already stated, there is in the upper part of the ore deposit, where oxidation prevails, abundance of ferric sulphate and sulphuric acid. A little salt, $NaCl$, or other chloride, is generally present. The H_2SO_4 , reacting upon $NaCl$, gives HCl , which in the presence of MnO_2 gives nascent chlorine, which dissolves gold. Some manganese goes into solution as sulphate, but certain higher manganates are possibly formed as well.

b) This chemical system will move downward under hydrostatic head. If it comes into a zone containing pyrite it will react upon the pyrite, and in the oxidation of the latter more iron sulphates and acid will be formed. If manganese dioxide is present, or if permanganic acid has been formed, no gold will be precipitated, and the system, with gold still in solution, will move to greater depths before ferrous sulphate can become effective.

c) But as the system moves downward, where no new sources of oxygen are available, the excess of acid is removed. There are

many ways by which acidity is reduced along with these reactions, but the principal one is probably the kaolinization of sericite and feldspar. In these reactions sodium, potassium, calcium, magnesium, and other sulphates are formed from acid and silicates; the silica remaining as SiO_2 and kaolin; the alkalies and alkalic earth sulphates going into solution. As the acidity decreases, iron and manganese compounds tend to hydrolyze and deposit oxides. At this stage of oxidation FeSO_4 becomes increasingly prominent, and not only completely inhibits further solution of gold but becomes increasingly effective as a precipitant. Thus manganite is probably precipitated with gold. The fractures in the primary pyritic gold ore below the water level thus become coated with a manganiferous gold ore, which may be very rich. The excess of oxygen which the system has carried down is used up in the manner indicated, and in this process limonite is formed, consequently the manganiferous gold ore deposited in the fissures and cracks contains kaolin and iron as well as manganese oxides.

2. *The oscillating, descending, undulatory water-table.*—The terms "water-table" and "level of ground-water" are generally used to describe the upper limit of the zone in which the openings in rocks are filled with water. This upper limit of the zone of saturation is not a plane, but a warped surface. It follows in general the topography of the country, but is less accentuated. It is not so deep below a valley as below a hill, but it rises with the country toward the hilltop and in general is higher there than in the valley. Nor is it stationary. In dry years it is deeper than in wet years, and in dry seasons it is deeper than in wet seasons. The difference of elevation between the top of this zone in a wet year and in a dry year is normally greater under the hilltop than on the slopes and in the valleys. In mines where the ground is open the level of ground-water probably changes with every considerable rain. Consequently, there is a zone above ground-water in dry periods but below it in wet periods, and in hilly countries this may be of considerable vertical extent. Thus the water-table oscillates, though in general moving downward with degradation of the land surface. It is in this zone of oscillation of the water-table that chemical activity is most varied. Without any change

in the character of the drainage or of the more constant conditions controlling the water-circulation, the chemical composition of the solutions affecting this zone may change from season to season. They may at one time be ferric sulphate or oxidizing waters, and at another time ferrous sulphate or reducing waters, since, after a wet season, the ferrous sulphate waters from below would tend to rise, after dilution with fresh water added by the rains. Consequently, the minerals of this zone may include, besides the residual primary and secondary sulphides, the oxides, native metals, chlorides, etc. Between the top of this zone and the surface or the apex of the deposit chemical activity is probably slow, because there is a scarcity of sulphides and other easily altered minerals to supply the salts upon which the chemical activity of ground-water in a large measure depends. As the country is eroded, this zone also descends; and if a mineral or metal persists long enough, the upper limit of the zone of active change passes below it, and may ultimately be exposed at the outcrop.

3. *The several successive zones in depth.*—As shown by S. F. Emmons, W. H. Weed, and others, many lodes, when followed from the surface down the dip, show characteristic changes. Below the outcrop, the upper part of the oxidized portion of the lode may be poor. Below this there may be rich oxidized ores; still farther down, rich sulphide ores; and below the rich sulphides, ore of relatively low grade. Such ore is commonly assumed to be the primary ore, from which the various kinds of ore above have been derived. The several types of ore have a rude zonal arrangement, the so-called "zones" being, like the water-table, undulatory. They are related broadly to the surface and to the hydrostatic level, but are often much more irregular than either; for they depend in large measure on the local fracturing in the lode which controls the circulation of underground waters. Any zone may be thick at one place and thin, or absent, at another. If these zones are plotted on a longitudinal vertical projection, it is seen that the primary sulphide ore may project upward far into the zone of secondary sulphides, or into the zone of enriched oxides, or into the zone of leached oxides, or may even be exposed at the surface. The zone of secondary sulphide enrichment (which is

not everywhere present) may project upward far into the zone of rich oxidized ore, or into the zone of leached oxides, or may outcrop at the surface. The zone of sulphide enrichment nearly always contains considerable primary ore, and very often the secondary ore is merely the primary ore containing in its fractures small seams of rich minerals. The zone of enriched oxides is generally found above the water-table when the latter is at the lowest, and often extends to the outcrop. In regions of rapid erosion, and especially of rugged topography, the conditions for the exposure of rich oxides, or even rich sulphides or primary ore, are more favorable. In places along the outcrop of a deposit where erosion is rapid the richer oxidized or sulphide ores may be exposed, whereas in other places, protected from erosion, and therefore exposed longer to solution, the same outcrop is frequently leached. It is evident that the amount of metal remaining in the upper part of the oxidized zone and at the outcrop depends upon the ratio between the rate at which the metal is dissolved, and the rate at which the valueless constituents are dissolved and removed. Under certain conditions gold is removed very slowly, and the removal of valueless constituents may effect a concentration at the very apex of the lode; while under other conditions, favorable to the solution of gold, it is removed more rapidly than silica, iron, etc., and the apex and the oxidized zone are leached. In a country not subject to erosion it would be supposed that the outcrops of manganeseiferous lodes would be everywhere leached; but rapid erosion may remove the upper part of the lode before it is completely leached, and, under favorable conditions, placers accumulate from the débris of the apex.

It thus appears that all of these zones except that of the primary ore are continually descending; so that ore taken from the outcrop may represent what was once primary ore; afterward, enriched sulphide ore; still later, oxidized enriched sulphide ore; later still, leached oxidized enriched sulphide ore; and finally become the surface ore. Through more rapid erosion at some particular part of the lode, any one of these zones may be exposed; and hence an outcrop ore of any character is possible. Consequently, longitudinal assay plans, showing the changes of value

in depth, though highly suggestive, and especially so when gold and silver are shown separately, are supplemented by studies of the paragenesis and by physiographic studies, in order that the approximate rate of erosion of the lode at various places may be known. In the absence of such knowledge, it is generally impossible to tell the genesis of a particular sample of ore from a mine. When all the data are assembled, however, greater confidence may be placed in the conclusion, since all the factors in the problem are intimately related.

4. *Criteria for the recognition of secondary enrichment.*—I shall not attempt to review all the criteria for the recognition of secondary enrichment. They involve practically all available data relating to the geology and physiography of a region, as well as the observed characteristics of its ore deposits. But each group of deposits may be studied with certain general criteria in view. Among these are: (1) the vertical distribution of the richer portions of the lode with respect to the present surface and to the level of ground-water; (2) the mineralogy of the richer and poorer portions of the deposit, and the character and vertical distribution of the component minerals; (3) the paragenesis, or the structural relations shown by the earlier ore and that which has been introduced subsequently.

In applying these principles, it should be remembered that circulation is generally controlled by post-mineral fracturing; that the changes depend upon climate and rapidity of erosion, and are affected by regional changes of climate, etc. Although the mineralogy of the ore is a useful aid, there are many minerals which are precipitated from cold solution and also from ascending hot solutions, and there are many others, the genesis of which is uncertain. Of the minerals formed in the zone of secondary sulphide enrichment, few, if any, are known positively to form under such conditions only. There are some, however, such as chalcocite and covellite, which nearly everywhere are clearly of secondary origin. Ruby silver is frequently, but not always, secondary. Other minerals, such as chalcopyrite, bornite, argenteite, etc., have no definite indicative value unless their occurrence suggests that they are later than the primary ore. Where minerals,

known to have formed elsewhere by processes of secondary sulphide enrichment, are clearly later than primary ore, there is a strong presumption that they were deposited by cold descending waters. If it can be shown, in addition, that they do not extend to the bottom of the mine, but are related to the present topography of the country, then this presumption may be regarded with considerable confidence as confirmed.

With respect to gold, the problem is difficult, because the native metal is the only stable gold mineral known to be deposited from cold dilute solutions. Consequently, the applicable criteria are limited; and the vertical distribution of the richer ore, though suggestive, is not in itself conclusive. Lindgren and Ransome, in their studies at Cripple Creek, have shown that the richer ore bodies may have in general a relationship to elevation, where there is little or no evidence of deep-seated secondary enrichment. The maximum deposition by ascending hot waters may be greater at one horizon than at another; and the rich ore, though showing broadly certain variations with depth, is in no way related to the water-table. If, however, it can be shown that rich seams of ore cross the primary ore and do not extend downward as far as the lowest level in the primary ore, but are related to the present topography of the country, and if it is known that the associated minerals which fill such openings are those which may be deposited by cold waters, the evidence of their secondary origin is practically conclusive. As already shown, seams of gold with limonite and manganese oxides occur in such relations. Similar ore frequently contains chalcocite and argentite also. Such occurrences could with great confidence be attributed to descending waters.

In the practical application of such reasoning to gold-bearing deposits it will sometimes be necessary to discriminate between the oxidized manganiferous gold ore which has resulted simply from the oxidation of a primary manganiferous ore like one containing rhodochrosite, and that which has been deposited in fractures in the sulphides lower down. In other words, it is desirable to know whether rich manganiferous ore in the upper part of a mine is residual from a primary ore body, and there-

fore will probably prove extensive, or represents the result of concentration under more deeply seated conditions after the manner indicated above. This discrimination may be easy in the sulphide zone, where the fractures with rich manganiferous ore are clearly shown; but in the oxidized zone one must rely upon the shape and distribution of the richer portions. If they are related to cracks in the mass of the oxidized ore, the inference is warranted, in the absence of other evidence, that they are residual secondary ore, and, being genetically related to the present topographic surface, are limited.

Native gold is, as already stated, the only gold mineral which is deposited by cold solutions. But native gold is deposited by primary processes also, and is by far the most abundant gold mineral so deposited. Consequently, in distinguishing between primary gold and gold deposited by cold solutions, one must rely upon associated minerals. When secondary chalcocite or certain secondary silver minerals are deposited, the attendant reactions precipitate gold. Consequently, the richer bunches of gold ore in the oxidized zone, residual from secondary ore formed under the deeper-seated conditions, may carry also considerably more copper and silver than the primary ore. But copper, and (unless cerargyrite is formed) silver also, are more readily leached than gold, even when manganese is present. Hence, the evidence of this character may have been destroyed.

With respect to other minerals associated with the secondary gold ore, we are not warranted, in the present state of our knowledge, in drawing definite conclusions. From the nature of the reactions, I think it may be possible to show that manganite, $Mn_2O_3 \cdot H_2O$, is, under conditions of incomplete oxidation, more often associated with the rich gold in such relations than pyrolusite, MnO_2 ; for, as already observed, the lower oxide is more likely to be precipitated than the higher, when secondary gold is deposited under deep-seated conditions. But under oxidizing influences the manganese oxides change their character so readily that this criterion, if it has any value, is probably not applicable to ores in the upper part of the oxidized zone, where they have been exposed to more highly oxygenated waters for a longer time. I

make these suggestions with respect to the character of the manganese oxides associated with the rich ore, not because I think the reactions which precipitate manganese are well enough understood to give a positive paragenetic value to the oxidized manganese minerals themselves, but in the hope that others will ascertain and report the character of the manganese oxide associated with gold in the deeper zone and in the residual products from that zone.

5. *Lateral migration of manganese salts from the country rock to the ore.*—Clarke's analyses¹ show that igneous rocks carry an average of 0.1 per cent of manganese oxide, and many basic rocks carry from 0.2 to 0.9 per cent. Where basic dikes have cut an ore body, they doubtless contribute manganese to the waters circulating in the deposit. The ore of the Haile mine, in South Carolina, is cut by basic rocks; and the ore bodies of the Delamar mine, in Nevada, are crossed by a basic dike. Both of these deposits show secondary enrichment of gold; and in both the better ore is found along the dikes. In general, however, the manganese from the country rock cannot safely be assumed to have migrated extensively into the ore deposit, for many analyses of mine waters do not show manganese; but where manganiferous rocks are intimately fractured and filled with seams of ore it would be supposed that the reactions requiring manganese could take place.

In my own experience I have found only trivial stains of manganese in those lodes where it was not present in the gangue of the primary ore; and, in view of its wide distribution in igneous rocks, I believe that the lateral migration of manganese into the ore under the conditions which generally prevail is very subordinate. Though the amount so contributed may facilitate the solution of gold, it is probably inadequate to form sufficient higher manganates or similar salts to suppress effectively the action of ferrous sulphate. Under such conditions the gold could not travel to the reducing-zone below the water level, but would be precipitated practically at the place where it had been dissolved.

6. *Concentration in the oxidized zone.*—The concentration of gold in the oxidized zone near the surface, where the waters

¹ *Bulletin No. 330, U.S. Geological Survey* (1908).

remove the valueless elements more rapidly than gold, is fully treated by T. A. Rickard in his paper on the "Bonanzas in Gold Veins."¹ Undoubtedly this is an important process in lodes which do not contain manganese, or in manganiferous lodes in areas where the waters do not contain appreciable chloride. In the oxidized zone it is sometimes difficult to distinguish the ore which has been enriched by this process from ore which has been enriched lower down by the solution and precipitation of gold, and which, as a result of erosion, is now nearer the surface. It cannot be denied that fine gold migrates downward in suspension; but in all probability this process does not operate to an important extent in the deeper part of the oxidized zone. If the enrichment in gold is due simply to the removal of other constituents, it is important to consider the volume- and mass-relations before and after enrichment, and to compare them with the present values. In some cases, it can be shown that the enriched ore occupies in the lode about the same space as was occupied before oxidation. Let it be supposed that a pyritic gold ore has been altered to a limonite gold ore, and that gold has neither been removed nor added. Limonite (sp. gr. from 3.6 to 4), if it is pseudomorphic after pyrite (sp. gr. from 4.95 to 5.10) and if not more cellular, weighs about 75 per cent as much as the pyrite. In those specimens which I have broken, cellular spaces occupy in general about 10 per cent of the volume of the pseudomorph. With no gold added, the ore should not be more than twice as rich as the primary ore, even if a large factor is introduced to allow for SiO_2 removed and for such cellular spaces.

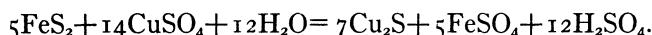
Rich bunches of ore are much more common in the oxidized zone than in the primary sulphides of such lodes. They are present in some lodes which carry little or no manganese in the gangue, and which below the water level show no deposition of gold by descending solutions. Some of them are doubtless residual pockets of rich ore which were richer than the main ore body when deposited as sulphides, but others are doubtless ores to which gold has been added in the process of oxidation near the water-table by the solution and precipitation of gold in the presence of the

¹ *Trans.*, XXXI, 198-220 (1901).

small amount of manganese contributed by the country rock. In view of the relations shown by the chemical experiments it is probable that a very little manganese will accomplish the solution of gold, but that it requires considerably more manganese to form appreciable amounts of the higher manganese compounds which delay the deposition of gold, suppressing its precipitation by ferrous sulphate. In the absence of larger amounts of the higher manganese compounds, the gold would probably be precipitated almost as soon as the solutions encountered the zone where any considerable amount of pyrite was exposed in the partly oxidized ore. From this it follows that deposits showing only traces of manganese, presumably supplied from the country rock, are not enriched far below the zone of oxidation.

7. *Vertical relation of deep-seated enrichment in gold to chalcocitization.*—In several of the great copper districts of the West gold is a by-product of considerable value. In another group of deposits, mainly of middle or late Tertiary age and younger than the copper deposits, silver and gold are the principal metals, and copper, when present, is only a by-product. But in some of these precious-metal ores chalcocite is, nevertheless, the most abundant metallic mineral, often constituting 2 or 3 per cent of the vein matter. Frequently it forms a coating over pyrite or other minerals. Some of this ore, appearing in general not far below the water-table, is fractured, spongy quartz, coated with pulverulent chalcocite. It frequently contains good values in silver, and more gold than the oxidized ore or the deeper-seated sulphide ore. Clearly, the conditions which favor chalcocitization are favorable also to the precipitation of silver and gold.

The exact chemical reaction which yields chalcocite is not known. At 100° C., according to Dr. H. N. Stokes,¹ the reaction with pyrite is probably about as follows:



In the cold, the reaction may differ in details, but without doubt much ferrous and acid sulphate is set free. Attendant reactions

¹ Unpublished MSS quoted by Lindgren in *Professional Paper No. 43, U.S. Geological Survey*, 183 (1905), and in Weed's translation of Beck's textbook.

confirm this statement; for, if calcite is present, gypsum is formed by the reaction of H_2SO_4 on lime carbonate; and, if the wall-rocks are sericitic, kaolin is formed by the acid reacting upon silicates, the potash going into solution as sulphate. The abundant ferrous sulphate must quickly drive the gold from solution, and it apparently follows that there may be no appreciable enrichment of gold below the zone where chalcocitization is the prevailing process.

VI. REVIEW OF MINING DISTRICTS

1. If gold is more readily dissolved in manganiferous deposits, it would be supposed that placers form less readily from pyritic manganiferous lodes than from lodes containing no manganese. If, in areas where the waters carry appreciable chlorine, placers have formed as extensively from such lodes as from lodes free from manganese, then the hypothesis fails.

2. The manganiferous lodes, in areas of chloride waters, as in the undrained areas of the Great Basin, should in general show less gold at the outcrop and in the upper portion of the oxidized zone than below. In silver-gold deposits, however, silver, on account of the insolubility of the chloride, may remain, or be concentrated, in the oxidized manganiferous zone. Bunches of rich gold ore carrying oxidized manganese in the oxidized zone are not necessarily fatal to the theory; for, as already stated, these are probably residual from the zone of secondary enrichment. An extensive enrichment in gold of the oxidized manganiferous ores at the surface, which are shown not to be residual from the zone of secondary ores, would indicate that the selective processes lack quantitative value, if the waters carry chlorine, and if the primary ores, from which the manganiferous oxidized ores are derived, carry appreciable pyrite to supply sulphate.

3. If in certain lodes gold migrates below the water-table, it should be precipitated quickly by ferrous sulphate. But MnO_2 converts ferrous sulphate to ferric sulphate, which does not precipitate gold. Hence, MnO_2 favors the solution of gold, and converting the ferrous salt to ferric sulphate removes the precipitant. Consequently, if auriferous lodes show enrichment in

the deeper zone but related to the present surface of the country, the manganiferous lodes should, the other favorable conditions provided, show greater differences in values with respect to gold than lodes free from manganese.

Gold provinces of the United States.—As Lindgren¹ pointed out in 1902, the principal gold deposits of the United States may be divided into four groups. The deposits of each group belong mainly to one metallogenetic epoch, and certain relationships are clearly shown. This classification, which has thrown much light on the genesis of the deposits, is useful as an instrument for study and for comparison of the deposits with respect to the problem of the migration of gold in them.

1. The Appalachian gold deposits, and those of the Homestake type in South Dakota, are the most important representatives of the oldest group. These deposits generally yield placers, are usually low grade below the water level, and are singularly free from bonanzas. They are, in general, not greatly leached near the surface, and may have been enriched by the removal of other material more rapidly than gold. At only one of them, the Haile mine, in South Carolina, it is thought probable that gold has been carried below the water level. Judging from descriptions, practically all of these deposits are free from manganese.

2. The California gold veins and related deposits in Nevada (Silver Peak) and in Alaska (Treadwell, etc.) are younger than the Appalachian deposits, and were probably formed in the main in early Cretaceous times. These deposits, where physiographic conditions are favorable, have generally yielded rich placers. At many places, moreover, the ore is worked at the very surface, and, there is very little evidence of the migration of gold to the deeper zones. In the places where detailed work has been done, rhodochrosite is never a gangue mineral, although manganese oxide does occur in traces in the country rock, and rhodochrosite is found in a few places in veinlets in the mining districts but not associated with the gold veins.

3. The deposits of the third group are later than the early

¹ "The Gold Production of North America," *Trans.*, XXXIII, 790-845 (1903); "Metallogenetic Epochs," *Economic Geology*, IV, No. 5, 409-20 (Aug., 1909).

Cretaceous, and some of them are probably early Tertiary. They are extensively developed in Montana, Nevada, Utah, and Colorado. Mr. Lindgren calls this group the Central Belt. Many of its deposits have yielded considerable gold, and in certain other districts very closely related genetically (Butte, Georgetown silver-gold lodes, Cortez Nevada, Tintic, etc.) much gold has been obtained as a by-product to copper or silver mining. Some of these deposits have yielded placers and some have not. At Philipsburg and Neihart, Mont., Georgetown, Colo., and elsewhere, the deposits show a secondary enrichment of silver below the water-table. At Philipsburg, and probably at some other places, an enrichment in gold accompanies this concentration of silver. Some of the lodes of group 3 carry much manganese, and some carry none. Present data are meager for most of these districts. The determination of gold from the surface down in a large number of deposits would serve as a useful check to the conclusions based upon the chemistry of the processes involved in its solution and precipitation.

4. Group 4 includes the most recent ore deposits in the United States. All of them are Tertiary, and most of them are Miocene or Pliocene. In general, they were formed relatively near the surface, and in some places it is highly probable that not more than a thousand feet of vein material has been removed by erosion since the ores were deposited. The majority of these deposits carry silver, and in many of them its value is greater than that of the gold; but they have supplied, notwithstanding, about 25 per cent of the gold production of North America. They are typically developed in Nevada (Comstock, Tonopah, Goldfield, Tuscarora, Gold Circle); California (Bodie); Idaho (De Lamar); South Dakota (later than Homestake type); Colorado (Cripple Creek, Idaho Springs, Rosita Hills, San Juan, etc.); Montana (Little Rockies, Kendall, etc.). Many occurrences in Mexico should probably be placed here, also. The deposits of this group have not supplied much placer gold. Many of these deposits are in arid countries, where conditions for working placers are not favorable; but even those in well-watered districts supply relatively little placer gold. Manganese is abundant in some of

these deposits (Comstock, Exposed Treasure, Tonopah); it is very sparingly present in others (Little Rockies); in still others (Goldfield) it is almost entirely absent.

A few small placers are associated with the manganiferous lodes, although at some places they seem to have been derived from veins near by which are not manganiferous. Many of the California veins carry rich ore at the very surface, but the Tertiary gold veins are generally richer in gold a few feet below the surface than at the outcrop. Doubtless, many of them would have been overlooked if it had not been for the concentration of horn silver and argentiferous pyromorphite at the surface.

It thus appears that practically all of the manganiferous gold deposits of the United States, so far as they have been described, may be included in groups 3 and 4; that nearly all described deposits where relations indicate a migration of gold belong to the same groups; that placers are much less abundantly developed than in groups 1 and 2; and that outcrops less frequently supply gold; that secondary enrichment below the water-table, if carried on at all, proceeds with extreme slowness in groups 1 and 2, but may be more pronounced in deposits of groups 3 and 4. Not all deposits of 3 and 4 carry manganese, however, and those which do not carry it show relationships more nearly approximating those which hold in the California gold veins. The migration of gold in the more important auriferous deposits of the United States is discussed in some detail in *Bull. 46, Amer. Inst. Mining Engineers*, 817-37.